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High-precision, *in situ* aircraft measurements of HCl and O_3 are used to quantify

stratospheric ozone that has been transported to the troposphere.

**A chemical ionization mass spectrometry (CIMS) technique has been developed for
precise *in situ* measurements of hydrochloric acid (HCl) from a high-altitude
aircraft. In measurements at subtropical latitudes, minimum HCl values found in
the upper troposphere (UT) are often near or below the 0.005-ppbv detection limit
of the measurements, indicating that background HCl values are much lower than a
global mean estimate. However, significant abundances of HCl were observed in
many UT air parcels as a result of stratosphere-to-troposphere transport events. A
method for diagnosing the amount of stratospheric ozone in these UT parcels was
developed using the compact linear correlation of HCl with ozone found throughout
the lower stratosphere (LS). Expanded use of this method will lead to improved
quantification of cross-tropopause transport events and validation of global
chemical transport models.**

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1 O_3 that is produced in the stratosphere and transported into the upper troposphere (UT) is a significant but uncertain contribution to the tropospheric ozone budget (*1-5*). The increase in tropospheric ozone (O_3) in the industrial era is a key term in the radiative forcing of climate change (*1, 2*). A variety of chemical transport models (CTMs) predict a range of total stratosphere-to-troposphere transport of O_3 that varies by more than a factor of three on a global annual basis (*1, 3*). Developing an accurate description and quantification of stratosphere-to-troposphere transport in CTMs is required before an adequate accounting can be made of present and future UT ozone abundances. Until now, no experimental technique could reliably quantify stratospheric ozone in the UT, particularly if significant mixing has occurred with background tropospheric air.

2 Long-lived gases (tracers) and correlations between tracers are often used to identify air parcels which have recently crossed the tropopause and to bound the net flux into the troposphere and stratosphere of O_3 and other gases (*6-15*). However, results from studies using tracers such as carbon monoxide (CO) or beryllium-7 to identify stratospheric O_3 in UT air parcels are limited generally to being 'semi-quantitative' (*6-9*). The limitations arise in part from variable tropospheric sources of the tracer or the lack of a known, compact and linear correlation of the tracer with O_3 in the lower stratosphere (LS) (see discussion below). Here we demonstrate the suitability of HCl as a quantitative tracer of stratospheric O_3 in the UT using subtropical in situ measurements made over the United States in summer 2002.

3   HCl has four attributes that underlie the quantification of stratospheric O_3 in the UT and that, as a group, are not shared by any other tracer currently being measured in situ or remotely. The attributes are:

(1) HCl has no known, significant sources in the UT, nor is the abundance of HCl expected to be significant in the UT, apart from what is transported from the stratosphere. However, short-lived organic species transported from the surface may be a source under some conditions (*16*). There are important sources of HCl in the lower troposphere (*17,18*), but wet scavenging of HCl in clouds makes it unlikely that appreciable amounts of HCl reach the UT. The lack of a significant upper tropospheric source is an important attribute because such a source would create an ambiguity in the UT as to the origin of observed HCl.

(2) HCl (as well as O_3) has a photochemical lifetime on the order of weeks in the UT/LS (*SOM*) due in part to low UV fluxes and the long lifetimes of the primary halocarbon source molecules for HCl. With a long lifetime, HCl remains a good tracer of LS O_3 present in the UT until precipitation scavenging results in selective HCl removal from an air parcel.

(3) HCl has a compact, linear correlation with O_3 throughout the LS. The correlation occurs because HCl is produced in the middle and upper stratosphere in approximately the same region where O_3 is produced. The linearity of the correlation is the result of the long photochemical lifetimes of HCl and O_3 and the transport and mixing that occurs in the LS away from the production region (*10, 11*). A linear correlation is needed in the LS in order to define and minimize the

uncertainty in the quantification of stratospheric O_3 in the UT (see discussion below).

(4) Based on the present results, HCl now can be measured in situ with high precision (0.005 parts per billion by volume (ppbv)) and high spatial resolution (<1 km). No comparable HCl observations have been reported for the UT from either in situ or remote instruments.

4   HCl is measured using a chemical ionization mass spectrometry (CIMS) instrument (*20, 21*), which was flown on the NASA WB-57F high-altitude aircraft in July 2002. On the flights of July 29, and 31, (hereafter referred to as Flt. A and Flt. B, respectively) the CIMS was operated with a new ion chemistry scheme based on the SF_5^- reagent ion. The SF_5^- scheme was developed to obtain sensitive and selective measurements of HCl, HNO_3 and $ClONO_2$ in the atmosphere (Supporting Online Material (*SOM*) Text). The detection limit for HCl is 0.005 ppbv (1s, 1σ), with an overall accuracy of ±25% for values above the detection limit. Many other measurements were made simultaneously on board the aircraft. Those used here include O_3, tropopause height, total reactive nitrogen (NO_y), carbon monoxide (CO), water vapor (H_2O), condensation nuclei, and potential temperature (*19, 22*). The observations are compared to results from a 3-D global CTM, the Integrated Massively Parallel Atmospheric Chemical Transport (IMPACT) model (*3, SOM*).

5   ***HCl in the stratosphere*** Correlations of the HCl and O_3 measurements from Flts. A and B are plotted in Fig. 1 for altitudes between 11 and 18 km, for latitudes between 24

and 39°N. The HCl:O_3 correlations are compact and linear in the LS and extend into the UT for both flights. Linear fits are shown for the stratospheric data from each flight. The linear correlations in the LS, which are expected based on the long lifetime of each gas as discussed above, are produced by the effective mixing between end-member air parcels (*10, 11*). The most extreme end-members in this overall mixing process are located in the LS near the tropopause and at altitudes well above the LS observation region. End-member air parcels near the tropopause are formed, in part, from tropospheric air containing low O_3 (< 200 ppbv) and low HCl, which enters the stratosphere primarily from low latitudes (< 30°) (*23-25*). Differing amounts of tropospheric O_3 in the air that enters the LS will result in small differences in the O_3 intercepts of the extrapolated LS correlations. Small intercept differences are found here between Flt A and B (see insets in Fig. 1). The differences in the LS correlation slopes between the two flights in Fig. 1 are consistent with the latitude dependence found in other observations and model results as discussed below.

6   IMPACT includes explicit treatment of chemistry and transport processes in the LS. The LS correlations in the model runs for late July 2002 show low variability at latitudes of 26°N and 46°N (Fig. 1C). These correlations include tropospheric values of O_3 since results are shown for altitudes above 9 km (~ 300 hPa). For comparison to the flight results, the IMPACT correlation fits are included in Fig. 1A and 1B. The excellent agreement found for the LS portion provides essential validation of the full stratospheric simulation in IMPACT.

7   Previously unpublished HCl:O_3 correlations from the Halogen Occultation

Experiment (HALOE) satellite dataset (*26*) in Fig. 1C also show that a linear correlation

between HCl and O_3 is ubiquitous in the LS. This dataset, as well as the IMPACT

results, shows a weak latitude dependence of the slope (*SOM*). HCl in the UT/LS region

has also been measured in situ (*27, 28*) and remotely by instruments on balloons (*29*) and

the Space Shuttle (*28*). None of these datasets has been used to examine the HCl:O_3

correlation in the UT/LS, or LS-to-UT transport. The HALOE dataset stands out among

the previous datasets because of its global coverage over more than a decade. The linear

fits to the HALOE data are offset (to higher HCl or lower O_3) with respect to both the

IMPACT model results and the in situ observations (*SOM*).

8   ***HCl in the troposphere*** Significant amounts of HCl were present in tropospheric

air parcels as shown by the green and blue data points in Fig. 1. The tropopause height

along the flight track, which is used to distinguish tropospheric from stratospheric air, is

derived from temperature soundings made onboard the aircraft (*22, 30*). Two features of

the tropospheric data are apparent. First, many air parcels have minimum HCl values

which are at or near the detection limit of 0.005 ppbv, implying that background HCl is

very low in the UT. Part of Flt. B (green points in Fig. 1) is particularly notable because

average HCl is 0.007 ± 0.005 ppbv over a horizontal distance of 300 km at 14 km

altitude. These observations alone suggest that large regions of the UT generally will

have HCl values much lower than 0.1 ppbv, which is a current budget estimate for

average free-tropospheric HCl (*17*). For the lowest HCl values in this study (< 0.02

ppbv), the associated O_3 values are less than 150 ppbv, which is consistent with values

expected from ozone sonde climatologies for the background UT (*31*). The second data feature is that the HCl:O_3 correlations in the tropospheric dataset are compact and essentially linear in both flights with slopes comparable to the LS correlations. These compact correlations provide strong evidence that the UT HCl values, which range up to nearly 0.1 ppbv, result from the transport of substantial amounts of stratospheric air and O_3 into the UT. The only other reasonable option, that being the mixing of near-surface source of HCl with an unspecified source of O_3, is implausible. In addition, the fact that no UT data points fall above the extrapolated stratospheric fit line is a further indication of the absence of a substantial HCl source in the background UT other than transport from the stratosphere.

9   The IMPACT results in Fig. 1C also show that the HCl:O_3 compact correlation extends below the tropopause (~ 200 ppbv O_3) and that low values (< 0.02 ppbv) of HCl are reached. The minimum model HCl values reached in observational area near Florida are <0.005 ppbv. These UT model features are highly consistent with those found in the observations. IMPACT uses a constant surface mixing ratio for HCl of 0.085 ppbv to simulate the surface source. Vertical profiles of HCl previously measured in the troposphere show elevated concentrations (up to 0.5 ppbv) near the surface due to localized sources and much lower levels (near 0.05 ppbv) at the 7-km upper limit of the measurements (*18*). A separate IMPACT simulation was conducted in which the contribution of surface HCl to the free troposphere was evaluated by doubling the imposed surface HCl mixing ratio. The resulting change in HCl in the UT was negligible

(*32*). This test indicates that wet deposition is very effective in the model in preventing

surface HCl from reaching the UT.

10   The HCl:O_3 correlation on Flt. A is contrasted with the correlations of O_3 with

NO_y, CO, H_2O and condensation nuclei in Fig. 2 . Several important points follow from

this comparison. First, these non-HCl tracers, which are routinely measured in situ, also

show compact correlations with O_3 in the LS (and therefore, also with HCl). In the UT,

the compactness of these other correlations is greatly reduced with non-HCl tracer values

exceeding those found in the LS. These changes are a result of the highly variable

tropospheric sources of NO_y, CO, H_2O, and condensation nuclei, respectively, which

create large values and spatial gradients of these tracers in the UT that are unrelated to

stratospheric intrusions. The changes in these non-HCl correlations exemplify, in part,

why they cannot be used routinely to quantify stratospheric O_3 in the UT with useful

accuracy. Second, the HCl:O_3 correlation contrasts sharply with those of the other

tracers, showing essentially no change in compactness between the LS and UT. If

significant HCl amounts were produced in the UT or transported from the surface to the

UT, a less compact HCl:O_3 correlation plot would be expected in the UT with data points

occurring in the shaded region in Fig. 2A. Third, the contrast in the compactness of the

UT correlations between HCl and the other tracers provides strong evidence that the UT

parcels in Fig. 2 result from mixing of stratospheric and tropospheric air and, hence, also

provides evidence that the transport of LS air to the UT is irreversible in this case.

Finally, the compact LS correlations of the non-O_3 tracers with HCl as implied by the

data in Fig. 2 could also be used to quantify stratospheric abundances of these non-O_3

tracers in the UT in manner similar to that described below for O_3.

11   *Quantifying stratospheric O_3 in the UT* In using HCl measurements to quantify

the amount of stratospheric O_3 transported to the UT or mixed into UT air parcels, two

key assumptions are required. First, the HCl/O_3 ratio is conserved during transport of

stratospheric air into the UT. This follows from the long photochemical lifetimes of both

tracers and the general absence of wet scavenging of HCl in stratosphere-troposphere

exchange events in the UT. Second, in the UT parcels under consideration, the amount of

HCl from non-stratospheric sources is negligible in comparison to that transported from

the LS. Here, the definition of stratospheric O_3 in the UT is O_3 that has recently been

above the thermal tropopause (*30*).

12   Based on these assumptions, the amount of stratospheric O_3 in a UT parcel is

expressed as:

$$\text{Stratospheric } [O_3] = [HCl_M] \bullet [O_{3,S}]/[HCl_S] \qquad\qquad (1)$$

where brackets indicate abundance, $[HCl_M]$ is the measured HCl in the UT parcel and

$[O_{3,S}]/[HCl_S]$ is the ratio of O_3 to HCl in the air parcel(s) that is the source of the

stratospheric O_3. This expression reflects the fact that HCl-containing air parcels

sampled in the UT are, in general, the result of a multi-stage mixing process between

parcel(s) of stratospheric air with parcel(s) of background tropospheric air (*Fig. 1 and*

SOM). The origin of the stratospheric air in a particular UT parcel influences the choice

of the $[O_{3,S}]/[HCl_S]$ ratio used in (1) for that parcel. For example, meteorological

trajectory analysis for Flts. A and B shows that stratospheric air entered the troposphere

over the Florida region throughout July through isentropic transport from higher latitudes

(*33*). As a consequence, the average $[O_{3,S}]/[HCl_S]$ ratio of 2250 from Flt. B, the higher

latitude flight, is chosen here to calculate the fraction of stratospheric O_3 for both flights

(see results below). A source of uncertainty in the $[O_{3,S}]/[HCl_S]$ ratio is associated with

the assumption of negligible background HCl in the UT. Although the observational and

model results suggest that background HCl values as low as 0.005 ppbv are common in

the UT, the true range and distribution of background values will not be known until

more extensive observations are made. A background HCl value equal to the detection

limit (0.005 ppbv) corresponds to a detection limit for stratospheric O_3 in Eqn. 1 of 11

ppbv. Based in part on this background value, the overall uncertainty in a stratospheric

O_3 value is estimated as the sum of ±15% and ±11 ppbv (*SOM*).

13   The stratospheric O_3 fractions for Flts. A and B are shown as vertical profiles in

Fig. 3. The UT data separate into two cases. The first case (blue points for Flts. A and

B) represents remnants of recent intrusions of mid-latitude stratospheric air into the UT

above Florida, as noted above. The fractions vary from 0.2 to 1 indicating a wide range

of irreversible mixing of UT and LS air. The error bars are examples of the estimated

uncertainties in the fraction. The second case (green points) represents UT air far from

the mid-latitude intrusions found over Florida, with fractions that vary over a narrower

range from zero to 0.4. This group includes the 300 km (31°-33°N) flight segment noted

above over which the average HCl amount was 0.007 ppbv. The vertical ranges in the

11

two cases are also distinct. In the first, the intrusion affects several kilometers below the tropopause. In the second, the influence of stratospheric O_3 is negligible a kilometer below the tropopause. The IMPACT model also shows a UT disturbance over Florida (*SOM, Fig. S1*), which is nominally consistent with the large stratospheric O_3 values in the first case. Although the model results are limited by low vertical resolution, this comparison provides a first order example of using in situ HCl observations to confirm stratosphere-to-troposphere exchange events and the accumulation of O_3 from such exchange in CTMs.

14   Quantifying stratospheric ozone in UT air parcels (as with Eqn. (1)) is distinct from, but related to, quantifying the amount of stratospheric air that is transported to the UT or mixed with UT air. A given amount of stratospheric O_3 in a UT air parcel can result from mixing with a small fraction of stratospheric air with high O_3 content or a larger fraction of stratospheric air with a lower O_3 content. Although the fraction of stratospheric air in a measured UT parcel cannot be determined from the HCl and O_3 measurements (since the particular stratospheric end member (s) involved in the mixing is unknown), an upper limit is given by assuming that the stratospheric end-member parcel has the lowest observed value of O_3, which is about 160 ppbv in this study. Values near this upper limit are more likely than lower values because stratospheric parcels with the lowest O_3 values are near the tropopause and, hence, are more likely to be involved in cross-tropopause intrusion and mixing events.

15   Stratospheric HCl molecules irreversibly mixed into the UT will be lost from an

air parcel after sufficient time through wet removal processes. Stratospheric O_3

molecules in the UT will participate in various photochemical cycles that might lead to

their destruction. The separate losses of HCl and O_3 from UT parcels represent a

limitation in using Eqn. (1) for long periods after an exchange event.

16   The ability of CTMs to resolve O_3 transport to the UT has improved considerably in

recent years (*34, 35*). For example, CTM analysis of the low latitude UT shows large-

scale intrusions of O_3 confirmed by lidar soundings (*34*). Based on the present study,

CTMs could be validated with greater precision and accuracy if suitable HCl

measurements are available either from in situ or possibly remote measurements.

Previously, no method could determine the stratospheric O_3 fraction reliably in the UT

when values varied widely from unity to near zero near the tropopause. Direct

comparisons of model results with estimates of stratospheric O_3 in the UT using high-

precision HCl observations, in addition to other tracer measurements, have great potential

to describe fine- and large-scale details of the exchange process. These details will

facilitate a resolution of the inconsistencies in global UT O_3 budgets regarding the

stratospheric source (*1*). The observations presented here constrain the UT HCl budget in

an unprecedented manner and indicate that background values in large regions of the UT

are much lower than published estimates. Global measurements of HCl and O_3 in the UT

will facilitate meaningful tests of the representation of stratospheric intrusions in CTMs

and will lead to improved estimates of HCl source strengths, transport processes, and

removal processes.

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22. NO_y: NO/O_3 chemiluminescence instrument (*37*); overall uncertainty is $\pm(15+9\%)$. H_2O: Lyman-α photofragment fluorescence hygrometer (*38*); accuracy is $\pm10\%$. CO: tunable diode laser absorption; precision is ±7.4 ppbv. CN: Nucleation-Mode Aerosol Size Spectrometer (*39*); combined uncertainty is $\pm 38\%$. Tropopause height: microwave temperature profiler (*40*); accuracy is 0.5 km. Temperature and pressure: aircraft probes; accuracy 0.5K and 0.5 hPa, respectively.

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30. A chemical or dynamical definition of the tropopause will give different, usually lower, tropopause heights than the thermal WMO definition (*41*). Here, the primary concern is to identify the stratospheric HCl/O_3 ratio. Since there will often be some tropospheric influence in the LS, choosing the highest commonly accepted tropopause value is the most reliable approach for determining the stratospheric HCl/O_3 ratio. Of the commonly used methods, the thermal tropopause has often

been the highest value (*41*).

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Supporting Online Material

SOM Text

Fig. S1

References

Figure 1. Correlations of measured and modeled mixing ratios of HCl and O_3. Data

points in panels **A** and **B** were acquired on two flights during the NASA Cirrus Regional

Study of Tropical Anvils and Cirrus Layers - Florida Area Cirrus Experiment

(CRYSTAL-FACE) mission based in Key West, FL, during July 2002. Both are five-

hour flights that sampled the UT/LS region up to altitudes near 18 km (200 – 70 hPa).

Aircraft data points are divided into groups for the stratosphere (red) and troposphere

(green and blue). The distinction between tropospheric and stratospheric data is based on

thermal tropopause height measured by remote temperature sounding onboard the

aircraft. The inset in each panel shows detail of the tropospheric data. The red lines in

panels **A** and **B** are unconstrained linear fits to the stratospheric data from Flts. A

(dashed) and B (solid), and have slopes of $(4.4 \pm 0.04) \times 10^{-4}$ and $(5.1 \pm 0.04) \times 10^{-4}$,

respectively. The CIMS HCl data were acquired at a rate of approximately 8 Hz during 3

s of every 12-s interval. The data points shown here are averages of each 3-s interval. A

spatial resolution of 0.6 km follows from the aircraft speed of approximately 200 m s^{-1}.

Panel A: Data from Flt. A (July 29, 2002), which was in the latitude range of 24 to 27°N

near Key West. The blue line is a linear fit to the IMPACT model results near Key West

(26°N, 280°E) from July 15 – August 1, 2002. **Panel B:** Data from Flt. B (July 31,

2002), which originated in Key West and covered latitudes from 24 to 39°N before

landing in Houston, TX (30°N). The blue points are tropospheric data from the first

flight leg (near Key West) and the green points are tropospheric data from the second leg

(near Houston). The green line is a linear fit to the IMPACT model results and is also

shown in panel **C**. Details of the tropospheric data are shown in the inset along with a

hypothetical mixing line (dotted black line) that shows that an arbitrary air parcel (HCl_M,

$O_{3,M}$) can be formed from mixing between two other air parcels: the stratospheric end member (HCl_S, $O_{3,S}$) and the tropospheric end member (0, $O_{3,T}$). The larger red point on the Flt. B fit line in the insets indicates the lowest stratospheric point used in the calculation of the stratospheric O_3 fraction. **Panel C:** Results from the HALOE satellite and from the IMPACT model. The HALOE data (black squares) are from the month of July for each of the years 1993 – 2003 for pressures between 83 and 35 hPa. The data were filtered to remove retrievals with anomalously high methane values (above 1650 ppbv) that skew the retrieved HCl values (*26*). The data are binned in 100 ppbv O_3 intervals and black error bars give the standard deviations in each bin. The black lines are linear fits to the HALOE data between 20 and 50°N (n, slope of $(5.4 \pm 0.17)\times10^{-4}$) and between 20°S and 20°N (○ , slope of $(3.9 \pm 0.15)\times10^{-4}$). The IMPACT results are averages from July 29 – August 1, 2002 at latitudes of 26°N (light blue line) and 46°N (green line) and longitudes between 255°E and 285°E. The error bars on the IMPACT fit lines are standard deviations for selected 100-ppbv O_3 bins. Only model results from altitudes above 9 km (300 hPa) and with less than 600 or 1000 ppbv O_3 are included to be consistent with the data from Flts. A and B, respectively. The model slopes are $(4.30 \pm 0.01) \times10^{-4}$ and $(4.81 \pm 0.01) \times10^{-4}$ for 26°N and 46°N, respectively.

Figure 2. Correlations of in situ measurements of HCl, H_2O, NO_y, CO and condensation nuclei with those of O_3, measured during Flt. A (*19, 22*). Data points for H_2O, NO_y, CO and condensation nuclei are shown only when simultaneous measurements of HCl are available. The data include both stratospheric (red points) and tropospheric (blue points)

samples. The distinction between stratosphere and troposphere data is based on the onboard remote sounding of the thermal tropopause height. The absence of data points in the shaded region of panel **A** is evidence of a negligible tropospheric background of HCl (See discussion in text).

Figure 3. Vertical profiles of measured HCl, O_3, and the calculated stratospheric O_3 fraction for Flts. A (top panels) and B (bottom panels). The dataset is identical to that used in Fig. 1. Each profile is shown with calculated potential temperature (left axis) and the approximate corresponding altitude (right axis). Potential temperature is derived from onboard temperature and pressure measurements. The data are shown for the stratosphere (red points) and the troposphere (green and blue points). The blue points in panels C and F are affected by a stratospheric intrusion. The intrusion was caused by flow around a quasi-stationary anticyclone that was located over the south-central U.S. for most of the month preceding Flts. A and B (*33*). The green points in panels D, E and F are from the second leg of Flt. B (covering a horizontal distance of about 300 km between 33°N and 31°N and just over 1 km below the tropopause) and correspond to the green points in Fig. 1B. The error bars in panels C and F are representative examples of the uncertainty in the calculated stratospheric O_3 fractions.
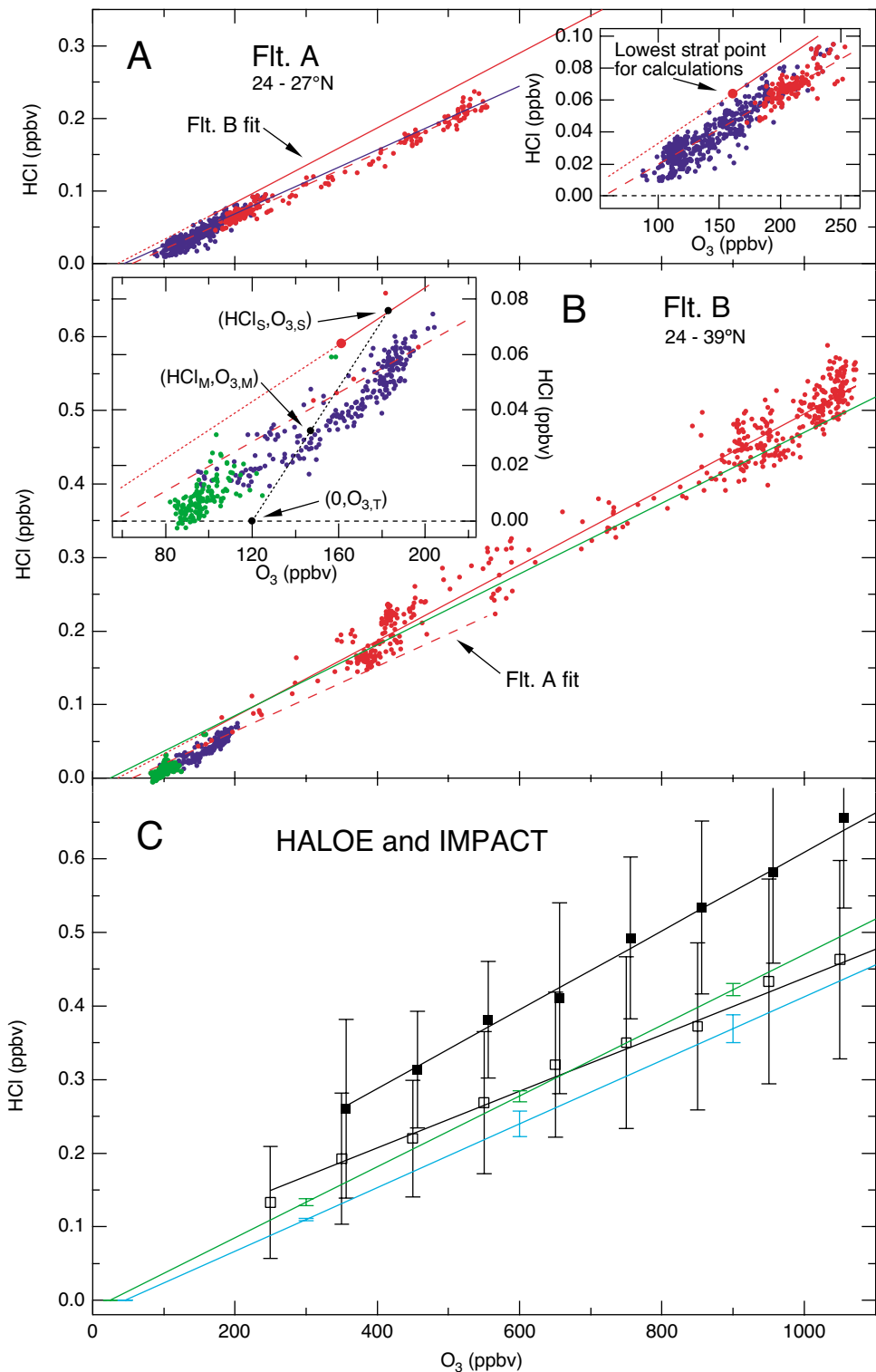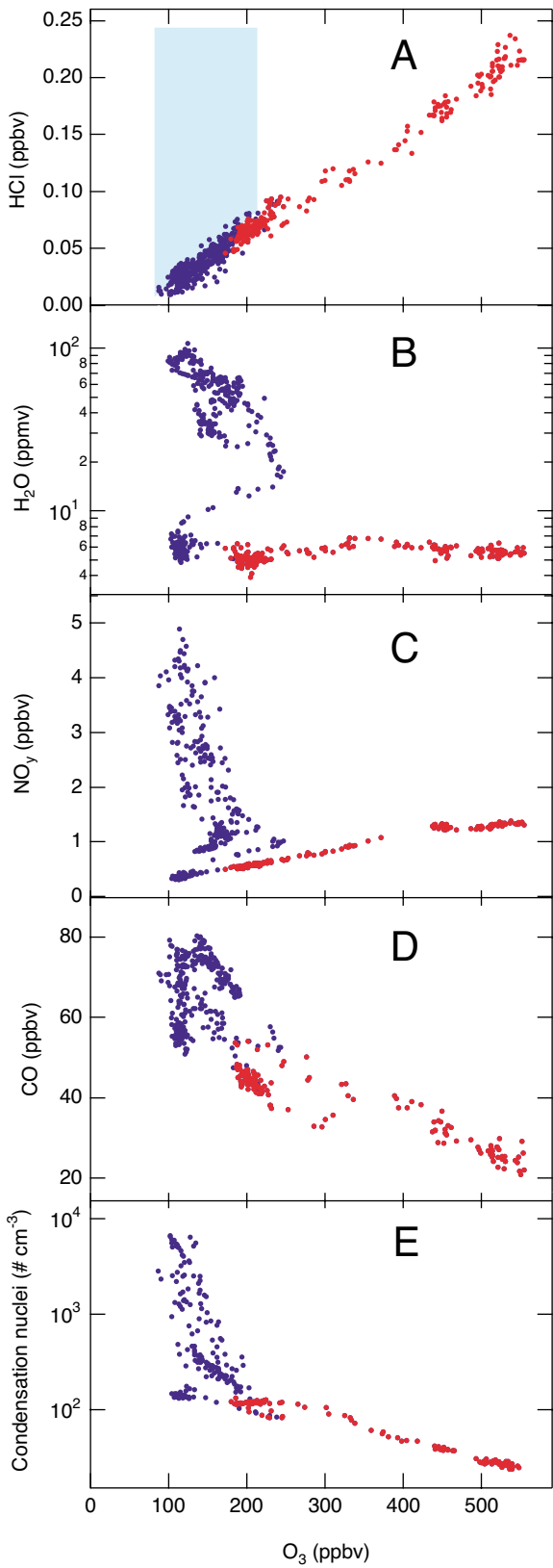
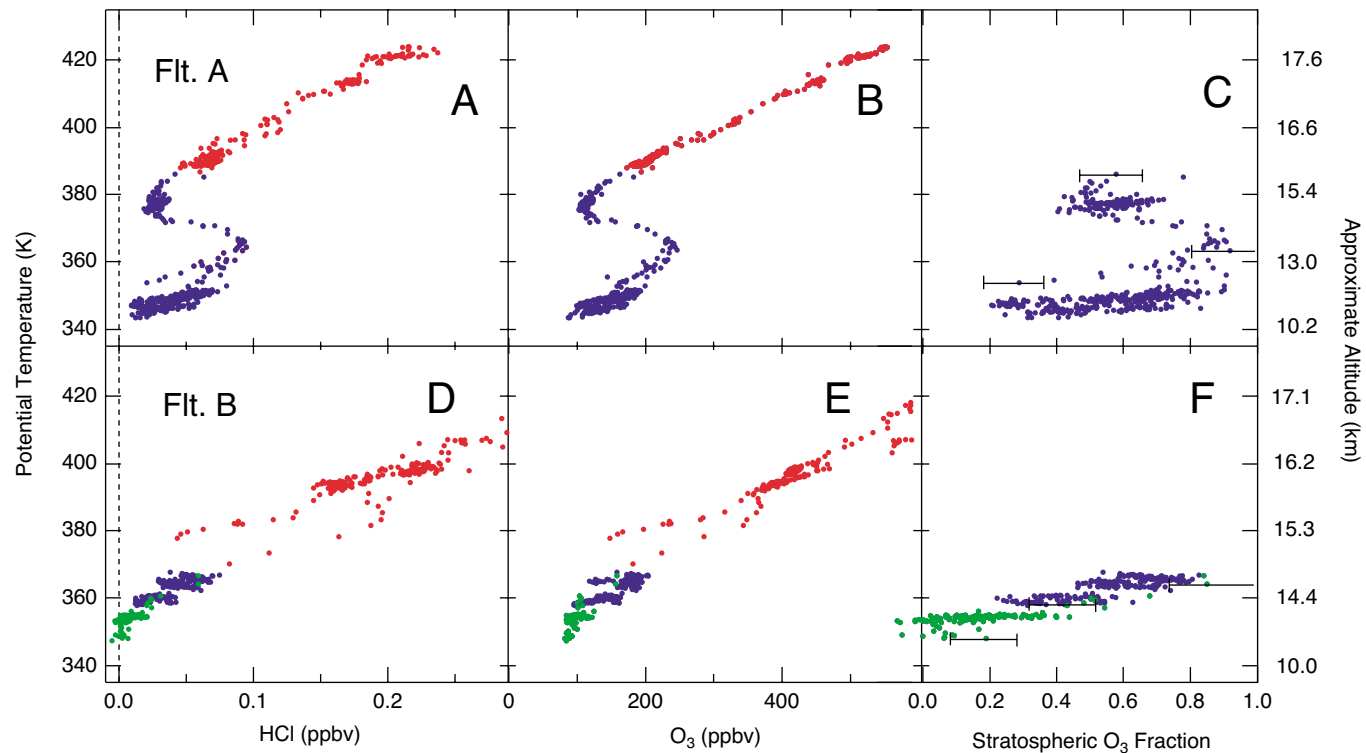**Figure 1** Marcy, et.al.

Figure 2 Marcy, et.al.

Figure 3 Marcy, et.al.

Supporting online material text for:

Quantifying Stratospheric Ozone in the Upper Troposphere Using *in situ*

Measurements of HCl

T. P. Marcy, D. W. Fahey, R. S. Gao, P.J. Popp, E. C. Richard, T. L. Thompson, K. H.

Rosenlof, E. A. Ray, R. J. Salawitch, C. S. Atherton, D. J. Bergmann, B. A. Ridley, A. J.
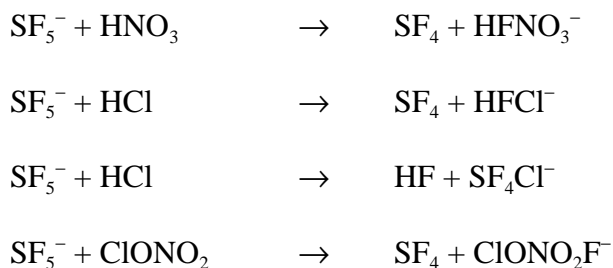
Weinheimer, M. Loewenstein, E. M. Weinstock, M. J. Mahoney

HCl lifetime

SP1   HCl is produced in the middle stratosphere, primarily from the ClO + OH reaction

and from the reaction of hydrocarbons with Cl radicals produced by UV photolysis of

halocarbon source molecules. At lower altitudes, the UV flux is diminished and the

lifetimes of the halocarbons increase, thus greatly reducing the source of HCl in the

UT/LS. The primary chemical loss processes of HCl in the UT/LS are the HCl + OH and

HCl + O reactions, both of which produce products that can react to reform HCl and,

thus, these processes do not constitute a substantial net sink for HCl. These loss

processes alone would give HCl a lifetime of over a month for typical UT/LS mid-

latitude conditions. HCl is also removed from the UT by precipitation scavenging, but

this process is ineffective in the low humidity conditions typical of the UT. In regions of

higher humidity lower in the troposphere, the HCl lifetime against removal by

precipitation scavenging will be much shorter.

The CIMS technique and SF_5^- chemistry.

SP2   CIMS has been used as a sensitive measure of nitric acid (HNO_3) and a number of other trace species in the atmosphere (*S1-10*). The CIMS technique employs reagent ions that react selectively with a neutral trace species of interest to produce a unique product ion, with minimal interference from other reactions. Measurements of the product ion abundance are used to quantify the abundance of the trace gas in atmospheric samples.

SP3   A new ion chemistry based on the SF_5^- reagent ion was developed in our laboratory to measure HCl, HNO_3 and $ClONO_2$ in the upper troposphere and lower stratosphere. The ion molecule reactions are as follows:

$$SF_5^- + HNO_3 \quad\rightarrow\quad SF_4 + HFNO_3^-$$

$$SF_5^- + HCl \quad\rightarrow\quad SF_4 + HFCl^-$$

$$SF_5^- + HCl \quad\rightarrow\quad HF + SF_4Cl^-$$

$$SF_5^- + ClONO_2 \quad\rightarrow\quad SF_4 + ClONO_2F^-$$

The $HFCl^-$ product ion is primarily used to measure HCl because it has much higher sensitivity to HCl than does SF_4Cl^-. The HCl values derived from the SF_4Cl^- and $HFCl^-$ measurements agree, thereby supporting the selectivity of the SF_5^- ion for HCl measurements.

SP4   Laboratory studies were designed to determine the suitability of the new chemistry scheme for airborne measurements and were carried out on a CIMS instrument

that is functionally equivalent to the flight instrument (*S1, S2*), but is arranged in a

configuration that allows relative ease of operation and modification. The sensitivity and

detection limit of the SF_5^- reagent ion scheme for HCl were determined to be

approximately 10^4 counts per second/ppbv and 0.005 ppbv (1σ, 1s), respectively,

allowing CIMS to measure any HCl value between the 3.5 ppbv maximum in the

stratosphere down to 0.2% of the maximum.

SP5   Laboratory tests were also employed to ensure that there is a well-defined

relationship between the measured product ion and the amount of HCl entering the

sample inlet of the system. In the case of the SF_5^- chemistry, the reaction rates are high

enough that the SF_5^- reagent ion could be significantly depleted by atmospheric levels of

HNO_3 and HCl, thereby causing a non-linear relationship between the product ion and

further addition of HCl or HNO_3. Accounting for this non-linearity required the use of a

somewhat more complicated mathematical relationship based on the known kinetics of

the reactions and verified by the tests in the laboratory.

SP6   A final concern for the suitability of the new ion chemistry scheme was that other

neutral species, such as water (H_2O) or O_3, might interfere in the detection of HCl by

reacting with the reactant our product ions noted above. Amounts up to 4 parts per

million by volume (ppmv) of O_3 and 100 ppmv of H_2O were added to the sample inlet in

the laboratory. This level of O_3, which is higher than would be encountered anywhere in

the UT/LS region, produced no significant interference with the HCl measurement. As

added H_2O approached 100 ppmv, there was a slight, but non-negligible effect on the

HCl measurement. The response means that ambient H_2O near or greater than 100 ppmv will interfere in the HCl measurement. For the data used in this study, H_2O values were below 100 ppmv (see Fig. 2).

SP7   The flight measurements of HCl were made simultaneously with HNO_3 measurements within 12-s intervals. The HNO_3 measurements were calibrated in flight by adding a known amount of HNO_3 to the sample flow from a permeation tube. The instrument was also zeroed in flight by adding dry N_2 in place of the ambient air sample. The ratio of HCl to HNO_3 sensitivities was determined by using the CIMS flight instrument in the laboratory and adding a calibrated flow of HCl to the sample flow. This ratio allowed the in-flight HNO_3 calibration to be used to calibrate the in-flight HCl measurements. A calibration method for $ClONO_2$ has not been fully developed.

IMPACT Model

SP8   IMPACT is a 3-D global CTM developed at Lawrence Livermore National Laboratory (*S11*). The model uses assimilated meteorological fields in simulating chemical and physical processes in the troposphere, stratosphere, and the climatically critical tropopause region. The model includes anthropogenic and natural emissions, advective and convective transport, vertical diffusion, dry deposition, wet scavenging, and both tropospheric and stratospheric photochemistry. The model results shown here are based on assimilated winds obtained from the NASA Data Assimilation Office (DAO) using the GEOS-3 model for 2002. The model was run for July 15 – August 1, 2002, with a grid resolution of 2º latitude $\times$ 2.5º longitude on 48 vertical levels and with

90 chemical species and 261 reactions. Although the model includes roughly 90% of the total organic Cl source gases, CFC-113 and HCFC-22 are not included. To account for this difference, the HCl model results shown here were increased by 10%.

HALOE Data

SP9   The latitude dependence of the HALOE slopes as shown in Fig. 1C is qualitatively consistent with the IMPACT results and with the aircraft observations. The seasonal change (April to October difference) in the HALOE HCl:O_3 correlation slope is small ($< 10\%$) at subtropical and mid latitudes (not shown). The maximum seasonal difference in the IMPACT model is about 20% at subtropical latitudes.

Quantifying Stratospheric O_3

SP10   A simplified example of the end-member mixing process that gives rise to HCl in UT air parcels is illustrated in the inset of Fig. 1B. When a stratospheric parcel (HCl_S, $O_{3,S}$) mixes with a tropospheric background parcel (0, $O_{3,T}$), a mixed UT parcel (HCl_M, $O_{3,M}$) is produced. The fraction of stratospheric air in this parcel is $[HCl_M]/[HCl_S]$ where the brackets indicate mixing ratio or abundance. The amount of stratospheric O_3 in the (HCl_M, $O_{3,M}$) parcel is $[O_{3,S}][HCl_M]/[HCl_S]$ or, equivalently, the stratospheric O_3:HCl ratio times the measured $[HCl_M]$ as:

$$\text{Stratospheric } [O_3] = [HCl_M] \cdot [O_{3,S}]/[HCl_S] \tag{1}$$

The possible stratospheric end members for the mixed parcel are any stratospheric parcel

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(a parcel that is above the thermal tropopause) on the chosen correlation fit line with an O_3 value greater than $O_{3,M}$. In this study, the end members of the chosen fit (Flt. B data) yield a range of 2000 – 2500 for $[O_{3,S}]/[HCl_S]$. The high end of this range comes from the lowest stratospheric point on the fit line, which occurs at approximately 160 ppbv O_3 (*38*). The low end of this range comes from a hypothetical point high on the fit line for which the ratio approaches the reciprocal of the slope of the fit line. This range of possible $[O_{3,S}]/[HCl_S]$ values along with the uncertainty of the stratospheric fit yields an uncertainty in the ratio of $\pm$ 15%. The choice of the stratospheric correlation to derive the $[O_{3,S}]/[HCl_S]$ ratio depends on the origin of the stratospheric air found in the UT, which, in turn, depends on the transport processes that are responsible for the particular intrusion of stratospheric air. Because of the complexity of such processes, the choice of correlation is an additional source of uncertainty in applying Eqn. (1).

SP11   By applying (1) to the HCl data in Figs. 3A and 3D using the average O_3:HCl ratio of 2250, the fraction of stratospheric O_3 in UT air parcels is calculated and plotted in Figs. 3C and 3F. For each tropospheric mixed parcel, ($HCl_M, O_{3,M}$), there is a set of $O_{3,T}$ values corresponding to mixing with the possible range of stratospheric parcels. For the datasets shown in Fig. 1, the range of $O_{3,T}$ values is between about 50 and 150 ppbv, which is consistent with values expected for background UT O_3 from O_3 sonde climatologies (*S12*).

SP12   At the points in the flight where the HCl is below the detection limit, the source of measured O_3 (within ±11 ppbv) is assumed to be the background troposphere. The 11

ppbv detection limit for stratospheric O_3, along with the lowest $[O_{3,s}]$ value of 160 ppbv, implies that less than 7% of the air in these parcels has recently come from the stratosphere. Alternatively, parcels with HCl below the detection limit might have been in the troposphere long enough to undergo precipitation scavenging of HCl, but not stratospheric ozone (19). In this case, the calculated stratospheric O_3 fraction represents a lower limit.

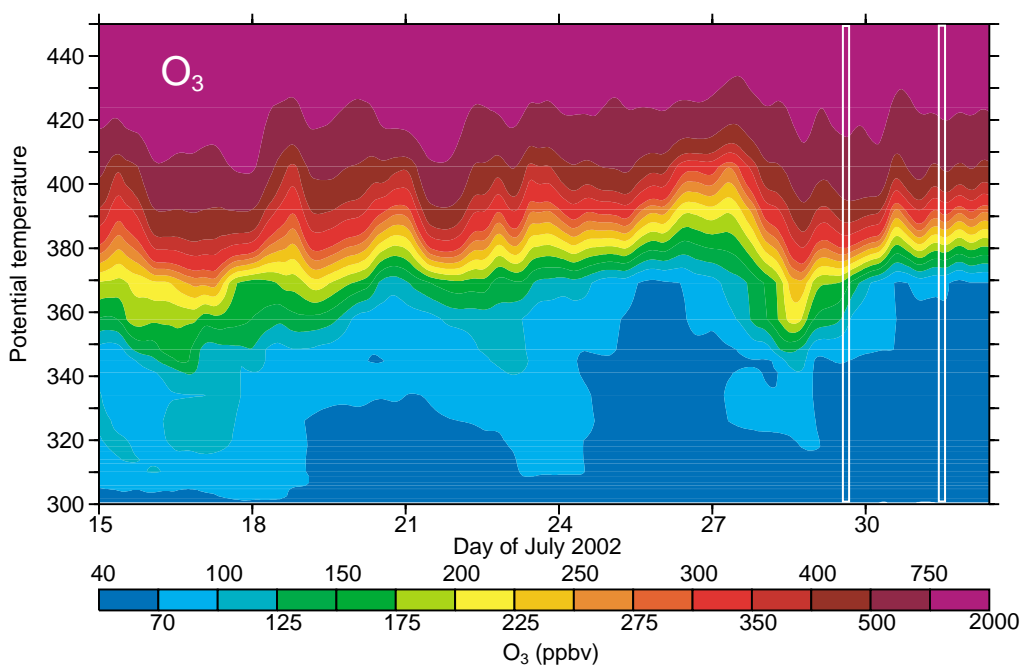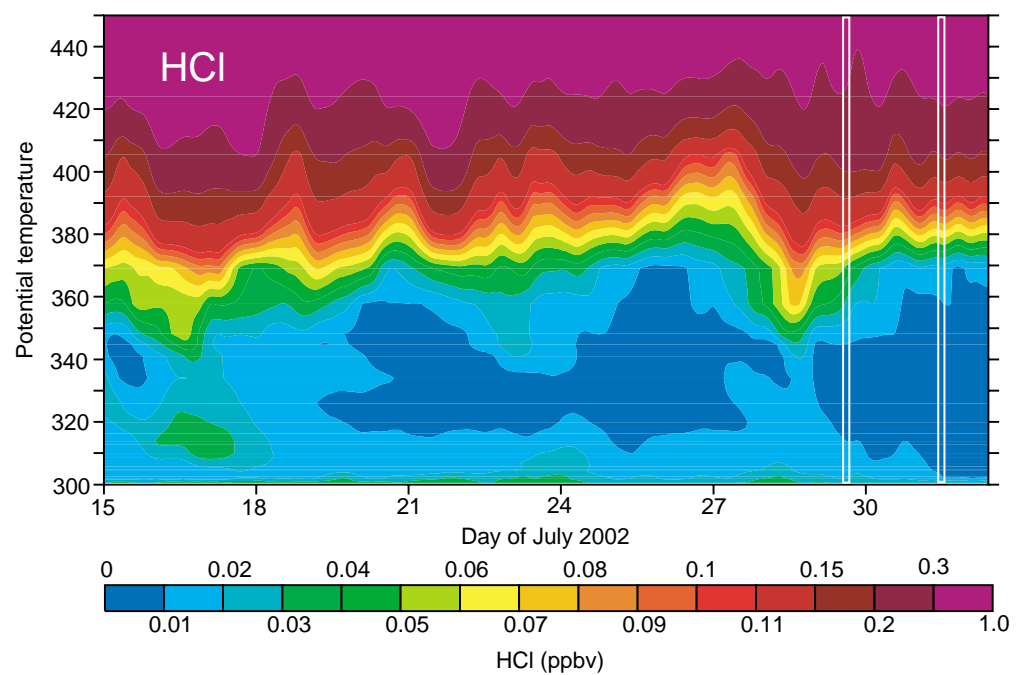Figure S1 Marcy, et.al.

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Figure S1. Results from the IMPACT model for HCl and O_3 as a function of potential temperature. The results are profiles from 26°N and 280°E for July 15 – August 1, 2002. The ticks for each day mark midnight GMT (0:00 Z). The white boxes in each panel show the flight times for Flt. A and B. HCl values are low (< 0.02 ppbv) and uniform throughout the subtropical mid-troposphere, above the influence of surface sources, over a several day period in July 2002. These low values are largely consistent with the Florida UT observations. The potential temperatures of the 200 ppbv O_3 and 0.06 ppbv HCl contours decrease from over 380 K at relatively undisturbed times to about 355 K near July 29th (Flt. A) and return to near 380 K by the 31st (Flt. B). These decreases are interpreted as an intrusion of stratospheric air into the troposphere based on other IMPACT model results that show air with elevated O_3 at 200 hPa approaching the Florida region from the northeast in the days preceding the 29th. Because these model simulations were run with limited horizontal (2° x 2.5°) and vertical resolution, changes in the 0.06 ppbv HCl contour in the model will not reproduce the detailed vertical structure in Flts. A and B as shown in Fig. 3. However, the potential temperature of both contours increase from Flt. A to B, roughly consistent with the model.

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